Red electroluminescence from a 1,4-diketopyrrolo[3,4-c]pyrrole (DPP)-based conjugated polymer

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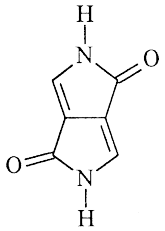
Abstract

A new hairy rod-type conjugated polymer consisting of alternating *N*-alkylated diketopyrrolopyrrole diphenylene and alkoxy-substitued phenylene units in the backbone is described. The polymer exhibits a characteristic bright red photo- and electroluminescence with maximum at about 640 nm. The luminescence behaviour is characterised in detail.

Keywords: Electroluminescence; Diketopyrrolopyrrole; Polymer light-emitting device; Hairy rod polymer

Organic pigments and dyes are traditionally used for colouring of fibres, plastics and surface coatings such as prints and inks. In recent times, however, organic colorants are finding increased use in the electronics industry, especially because of certain functional properties such as fluorescence, photoconduction, selective absorption of infrared radiation or possible electroluminescence (EL). Here particularly the so-called high-performance pigments with exceptional light, weather and heat stability are interesting candidates, among them being heterocyclic pigments [1,2] such as quinacridones, perylene derivatives and the more recently commercialised diketopyrrolopyrroles (DPP) with the pyrrolo[3,4-c]pyrrole-1,4-dione unit



as the underlying chromophoric system [3]. DPP derivatives are already used as pigments in conventional applications [4,5], while a number of electronic applications have recently been proposed, e.g. as charge generating materials for laser printers [6], information storage systems [7] and erasable optical memory devices [8]. Electroluminescent elements containing a fluorescent DPP derivative in the luminescent layer have likewise been claimed [9].

In order to fully exploit the photo- and electroactive properties of the colorants and to improve the processability into thin films often required for these applications, it is highly advantageous to use polymers with the chromophoric units covalently attached to or incorporated in the backbone. A number of publications was already concerned with DPP-containing polyesters [10], polyurethanes [10], dendrimers [11] and others [12,13] and even the preparation of DPP-containing conjugated polymers using the Stille [14] or Suzuki cross-coupling reaction [15] has been described. However, up to now, only photoluminescent [10,11,15] and photorefractive properties [14] were characterised in greater detail. Purpose of this study is to report on the synthesis and characterisation of a new DPP-containing conjugated polymer and to describe its application as active layer in a polymer light-emitting device (PLED). As recently reviewed [16,17], PLEDs offer significant advantage over other competing technologies, as they can be fabricated easily and cheaply, and the operational lifetime and power efficiency of such devices has meanwhile been optimised to a point, where a commercialisation seems feasible.

In our study, the DPP-based polymer **1** (Fig. 1) was used. **1** was prepared from 1,4-diketo-2,6-dihexyl-3,6-di(4-bromophenyl)pyrrolo[3,4-c]pyrrole **2** [15] and 2,5-diiso-pentoxybenzene-1,4-diboronic acid **3** [18] using

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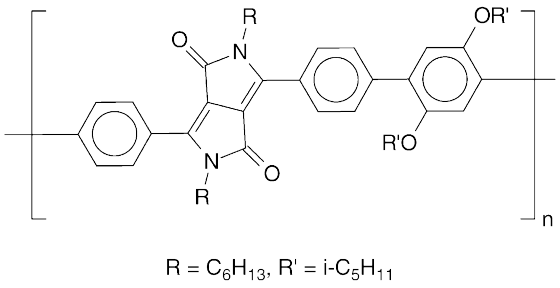


$R = C_6H_{13}$, $R' = i\text{-}C_5H_{11}$

Fig. 1. Molecular structure of polymer **1**.

the tetrakis(triphenylphosphino)-palladium(0)-catalysed Suzuki-type reaction [19,20]. **1** was obtained as a bright orange powder, which was soluble in common organic solvents such as chloroform or tetrahydrofurane. The weight average molecular weight was about 11.500, the polydispersity 2.4.

A solution of polymer **1** in chloroform exhibits a bright orange colour with red-orange fluorescence. The maximum absorption in the visible occurs at 503 nm (Fig. 2). Compared with monomer **2**, the maximum is red-shifted by 27 nm due to the more extended chromophoric system and the π-conjugated polymer backbone. An even stronger shift is found for the photoluminescence, the maximum of polymer **1** occurring at 570 nm and of the corresponding monomer **2** at 533 nm. The photoluminescence quantum yield of a polymer solution in $CHCl_3$ relative to Rhodamine 6G in ethanol [21] is 72%. Films of the polymer with thickness between 50 and 350 nm could be easily prepared by spin-coating of a chloroform solution onto quartz and ITO-coated glass substrates and subsequent evaporation of the solvent. Films of **1** exhibit an absorption maximum of 509 nm, quite similar to the solution, whereas the maximum of the photoluminescence appears at 640 nm (Fig. 3). The large red-shift might be explained in terms of interactions between transition moments of nearest-neighbour molecules in the solid-state [22]. In general, the optical spectra indicate

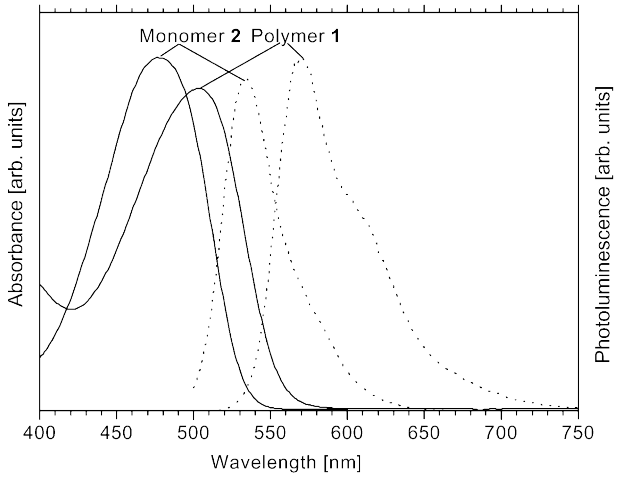


Fig. 2. Optical absorption (—) and photoluminescence (- - -) spectra of polymer **1** and monomer **2** in chloroform solution.

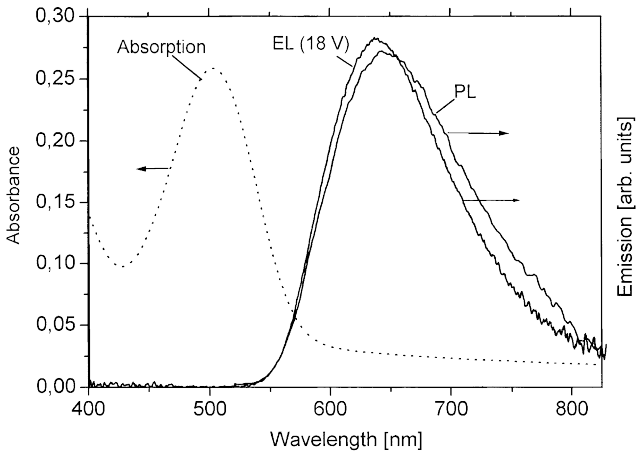


Fig. 3. Optical absorption, photo- and EL spectra of a thin film of polymer **1**. The EL spectrum was measured from an ITO/polymer/OXD7/Ca/Mg device at 18 V.

that the absorption and emission of the polymer are dominated by the DPP units. Presumably these units represent the part of the backbone with the lowest band gap so that the excited state becomes localised at these units, and their photoluminescence is strongly favoured.

To get information on the charge injection for the polymer, redox measurements of thin polymer films cast on a platinum electrode from chloroform solution were recorded using cyclic voltammetry. Polymer **1** possessed an irreversible oxidation peak at a potential of 1.01 V, the onset of the oxidation being located at 0.80 V when swept anodically. The onset potential is comparable to PPV (0.85 V) [23]. When swept cathodically, a reversible reduction peak was found at −1.45 V, the onset voltage being −1.04 V. This potential is clearly higher than that of PPV (−1.7 V) [23], i.e. polymer **1** has a higher electron affinity probably due to the presence of the electron accepting lactam units in the DPP chromophor. The HOMO/LUMO positions calculated from the corresponding onset voltages [24] are −5.3 and −3.5 eV with respect to the vacuum level. If ITO (indium tin oxide treated with oxygen plasma, bearing a work function of −4.9 eV [25]) is used as the anode the injection barrier for holes can be estimated to be 0.4 eV, and with aluminium as the cathode (work function −4.2 eV [26]) the injection barrier for electrons is 0.7 eV. These barriers are rather high, which implies that other electrode materials and/or additional charge and hole-injecting layers are needed in order to improve the flow of holes and electrons across the heterojunctions and thus to cause a sufficiently intense EL.

In order to investigate the EL properties of the polymer, two different devices were prepared. The first one was a single-layer device simply consisting of an ITO coated glass support, onto which the polymer was spin-coated and an aluminium electrode was evaporated. The ITO-layer served as the anode (hole-injecting electrode), the aluminium as the cathode (electron injecting electrode). The thickness of the individual layers of the ITO/polymer **1**/Al PLED is indicated in Fig. 4a. The figure also contains a representative plot of current

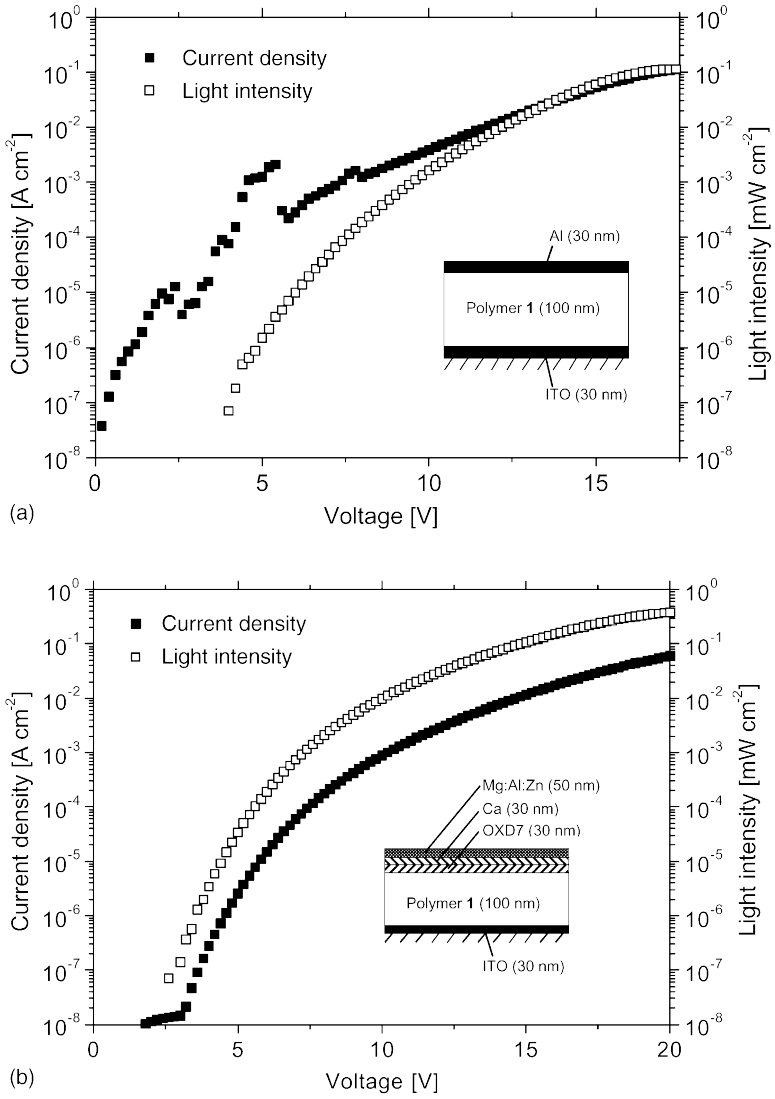
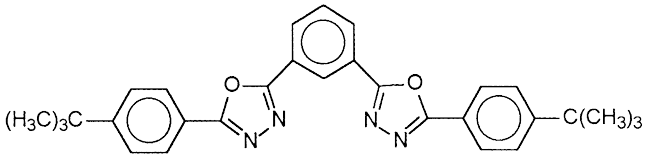


Fig. 4. Plot of current density and light intensity versus voltage of PLEDs containing **1**: (a) ITO/polymer **1**/Al; (b) ITO/polymer **1**/OXD7/Ca/Mg:Al:Zn.

density and output of light as a function of the applied voltage. The current shows considerable leakage for voltages between 0 and 5 V indicating that the polymer film quality needs further improvement. Nevertheless, the light output of the device shows a smooth behaviour. The turn-on voltage of the device, i.e. the lowest voltage at which an EL signal can be detected is 4 V. The light intensity increases with the applied voltage until at 17 V (current density 0.12 A cm^{-2}) a light intensity of 0.11 mW cm^{-2} is reached. The quantum efficiency of this device in its maximum is about 0.06% at 15 V.

In order to improve the electron injection into the polymer, a second device containing an additional electron conducting/hole blocking layer and a calcium electrode was prepared. The oxadiazole derivative OXD7 [27]



served as the electron conducting material, which was evaporated on top of the light-emitting polymer layer. The OXD7 layer was covered by a calcium electrode, which again was deposited by evaporation in vacuo. Finally, for protection of the calcium against air and humidity, an additional Mg:Al:Zn alloy layer was deposited as the uppermost layer. The structure of the resulting two layer device consisting of ITO/polymer **1**/OXD7/Ca/Mg:Al:Zn is schematically indicated in Fig. 4b together with data on the thickness of the individual layers. The figure also shows a representative plot of current density and light output as a function of the applied voltage. As can be seen, the turn-on voltage of the device is only 3 V. Increasing the voltage leads to an increasing intensity of the emitted light, until at 17.5 V an intensity of 0.20 mW cm^{-2}, and at 20 V (current density 0.06 A cm^{-2}) an intensity of 0.4 mW cm^{-2} is reached. At 20 V, the luminance is about 40 cd m^{-2} corresponding to a luminous efficiency of about 0.1 cd A^{-1}. Although the current density of this device is considerably lower than

of the previous one, the light intensity is significantly higher, and the maximum quantum efficiency is more than an order of magnitude higher (about 0.7% at 5 V decreasing to 0.4% at 20 V). This can be ascribed to the OXD7 layer and the calcium electrode. The electron injection layer reduces quenching effects at the metal electrode and favours radiative charge carrier recombination in the emitting layer, whereas the calcium electrode provides a more effective electron injection from the cathode into the organic material than the aluminium electrode.

The EL spectrum of polymer **1** measured from the ITO/polymer **1**/OXD7/Ca/Mg device is very similar to the photoluminescence spectrum of **1** (Fig. 3). Red light with maximum intensity in the wavelength region of 640 nm is emitted, the accurate maximum being somewhat dependent on the voltage applied. This may originate from a different extent or location of the recombination zone at different voltage. At 14 V, the maximum of the EL appears at 646 nm, at 18 V at 634 nm, and at 20 V, the maximum is found at 631 nm. The maximum position is comparable with poly(3-alkylthiophene) derivatives [28–30].

In conclusion, we have demonstrated that a conjugated hairy rod-type polymer consisting of diketopyrrolopyrrole and phenylene units in the backbone exhibits a red photoluminescence and EL. The polymer can also be looked at as a poly(1,4-phenylene), in which every fourth phenylene unit is replaced by a diketopyrrolopyrrole heterocyclic unit. The heterocyclic units clearly dominate the optical properties both in absorption and emission. The EL intensity of the polymer can probably be further enhanced by optimising the device structure concerning the electrode materials and the use of appropriate hole and electron conducting layers. Future work is therefore concerned with device optimisation as well as the search for other DPP-containing conjugated polymers with possibly even higher EL intensity.

Acknowledgements

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Appendix A. Experimental

A.1. Materials

1,4-Diketo-2,6-dihexyl-3,6-di(4-bromophenyl)pyrrolo[3,4-c]pyrrole **2** and 2,5-diiso-pentoxybenzene-1,4-diboronic acid **3** were prepared according to the literature [15,18]. 1,4-Diketo-3,6-di(4-bromophenyl)-pyrrolo[3,4-c]pyrrole was obtained from Dr. A. Iqbal, Ciba Specialty Chemicals, Basle (Switzerland). All starting reagents, solvents and catalyst were purchased from Fluka, Aldrich or Acros and used without further purification. The reactions were carried out under nitrogen.

*A.2. Preparation of polymer **1***

An amount of 1 mmol of **2** and 1 mmol of **3** were dissolved in 15 ml of THF under nitrogen. Fifteen millilitre of a solution of $NaHCO_3$ in water (2 M) and 12 mg of tetrakis-(triphenylphosphino)palladium(0) were added. Then the mixture was heated to 80 °C and stirred for 72 h. Subsequently the reaction mixture was cooled and the polymer was precipitated in methanol. The polymer was filtered off, washed with diluted hydrochloric acid, dissolved in chloroform and reprecipitated in methanol (M_w = 11500 g/mol).

UV ($CHCl_3$) 304 nm ($\varepsilon = 5.6 \times 10^4$ cm^2/monomol), 503 nm (21.3×10^4); ^{1}H-NMR ($CHCl_3$, 300 MHz, ppm) δ 7.85 and 7.50 (H of phenylene in DPP), 7.05 (H of substituted phenylene), 4.05 and 3.87 (α-CH_2), 2–0.4 (CH_2, CH_3); IR (KBr) (cm^{-1}): 2954 (s, ν CH_2, as), 2927 (s, ν CH_2, as), 2868 (m, ν CH_2, s), 1678 (s, ν C=O), 1607 (m, ν C=$C_{arom.}$), 1491 (m, ν C=$C_{arom.}$), 1465 (m, δ CH_2, CH_3), 1384 (m, δ CH3, s), 1207 (m, ν C–O), 1090 (m, ν C–O), 841 (m, δ C–$H_{arom.}$).

A.3. Methods

Molecular weights were determined using size exclusion chromatography (SEC) with a Waters/Millipore UV detector 481 and an SEC column combination (Latek/Styragel 50/1000 nm pore size). All measurements were carried out in tetrahydrofurane at 45 °C. The columns were calibrated versus commercially available polystyrene standards. UV/Vis-absorption spectra were taken using a Perkin Elmer Lambda 14 spectrometer. Fluorescence spectra were measured with a Perkin Elmer LS50B spectrometer. ^{1}H-NMR spectroscopy was carried out using a 300 MHz Bruker AC 300 spectrometer. Fourier transform infrared spectra were recorded using a Perkin Elmer spectrum 1000 spectrometer. EL spectra were determined with an Ocean Optics S2000 Fiberoptic spectrometer with CCD array and 600 lines/mm grating. The current–voltage characteristics and light intensities were measured simultaneously using a Keithley 236 source measure unit and an Si-photodiode connected to a Keithley 485 picoamperemeter. To collect all emitted light the sample was thereby put into an integrating sphere. To obtain absolute values of the emitted light intensity (mW cm^{-2}) the whole system of the integrating sphere and the photodiode were calibrated. Luminance measurements (cd m^{-2}) were performed at selected voltages using a Minolta CS-100 spot-photometer. The film thickness was measured with a Dectac Surface Profiler. Thin films were prepared from chloroform solution (15 mg/ml) using a

commercially available Hamatech spincoater (10 s at 1200 rpm, 20 s at 1700 rpm, 30 s at 1000 rpm). Cyclovoltammetric measurements of thin films of the polymer (cast from chloroform solution onto a platinum plate) were carried out in a three electrode glass cell with Pt working electrode, a platinum plate as counter electrode, and a standard calomel electrode as reference. An electrolyte solution of 0.1 M tetrabutylammonium perchlorate in anhydrous acetonitrile was used. Experiments were carried out at room temperature, the sweep rate was 5 mV/s (Heka potentiostat/galvanostat, model PG 390).

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